

## **Integrating Molecular Modeling and Process Safety Research**

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### ABSTRACT

The risk assessment of reactive chemicals or energetic materials is an important concern in chemical and petrochemical industries and is a key area of research at the Mary Kay O'Connor Process Safety Center (MKOPSC). The paper discusses applications of molecular modeling to obtain thermochemical data for reactive or hazardous materials and to predict calorimetric data based on molecular properties.

Hydroxylamine (HA) is an example of a highly reactive and poorly characterized compound with important industrial applications. The heat of formation for gaseous hydroxylamine under standard conditions is calculated, using isodesmic reactions at several levels of quantum chemical theories. To gauge the computed HA values, the gaseous hydrogen peroxide heat of formation is calculated by the same methods and compared with experimental data. Based on our calculations we recommend an average value of -11.4 kcal/mol for the gaseous HA heat of formation at 1 atm and 298.17 K.

The oxygen balance method, ASTM CHETAH, and the Calculated Adiabatic Reaction Temperature (CART) are a few of the theoretical methods that are commonly employed for reactive hazard evaluation. In an alternate approach, data obtained from calorimetric experiments and published kinetic parameters were correlated using calculated molecular properties. Quantitative structure-property relationships (QSPR) based on quantum calculations can be employed to correlate calorimetrically measured onset temperatures and heats of reaction with molecular properties. The primary objective is to extend and complement available experimental data with predictions for the species where no or few experimental data exist.

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## Introduction

The field of process-safety has evolved considerably since the catastrophic Bhopal accident in 1984 and today occupies an inseparable position in the chemical process industries (CPI). Incidents in the past few years have led to increased focus on improvements in reactive chemicals hazard assessment. Hazards posed by reactive chemicals or energetic materials under a variety of conditions must be properly understood and evaluated for safe working of a plant. We believe that molecular modeling can be effectively used to expedite reactive hazards assessment and perform detailed analysis on energetic substances without extensive testing.

Developing research in the field of molecular modeling is everyday taking us closer to a 'virtual laboratory' concept, where chemistry can be performed on a computer. Molecular modeling provides a unique approach for *a priori* prediction of hazards based on our understanding of a system. At the Mary Kay O'Connor Process Safety Center, we have employed a few of the available molecular modeling techniques to estimate thermophysical properties, investigate elementary reactions for HA decomposition, and to predict calorimetric data based on molecular structure alone. The paper will briefly discuss our results obtained employing *ab initio* techniques and outline few areas, where we believe molecular modeling can contribute significantly in improving safety of a plant.

The next section discusses the calculation of standard heat of formation for hydroxylamine and the reactions involved in its decomposition. This is followed by section on prediction of calorimetric data based on molecular structure using Quantitative Structure Property Relationships (QSPR).

## Research on hydroxylamine system

Hydroxylamine (HA),  $\text{NH}_2\text{OH}$ , has recently been involved in two major industrial incidents with disastrous consequences<sup>1,2</sup>. Calorimetric studies on aqueous solutions of HA indicate that it is a highly reactive compound<sup>3</sup>, but its properties are poorly characterized. Pure HA is known to explode at room temperature, and the decomposition of HA is extremely sensitive to metal contamination<sup>3</sup>.

### HA Heat of formation<sup>4</sup>

Since an accurate HA heat of formation value was not available, we employed theoretical calculations, mostly quantum chemical, for its estimation. Errors in absolute quantities from quantum chemical calculations are often systematic. To compensate for some of the systematic errors, isodesmic reactions, which conserve the number of each type of bond in reactants and products, are used to obtain more accurate heats of formation<sup>5</sup>. Here, the following isodesmic reactions were employed for HA:



To benchmark the computed HA values, the heat of formation for hydrogen peroxide, a similar species for which reliable experimental data are available, was calculated by the same methods and with the following isodesmic reaction:



The usual procedure for calculating the heat of formation value of an unknown compound is to combine the heat of reaction obtained from an isodesmic reaction with the experimental heat of formation values for the known compounds<sup>5</sup>. The HA heat of formation using Reactions (1), (2), and (3) were determined from the equations (4), (5), and (6), respectively, using the calculated heat of reaction,  $\Delta H_{\text{Rxn}}^{\text{Calc}}$ , and the experimental heats of formation values at 1 atm and 298.17 K for ammonia<sup>6</sup>, water<sup>6</sup>, and hydrogen peroxide<sup>7</sup> were taken as  $-10.98 \pm 0.084$ ,  $-57.7978 \pm 0.0096$ , and  $-32.58 \pm 0.05$  kcal/mol, respectively.

$$\Delta H_{\text{f, NH}_2\text{OH}} = \Delta H_{\text{f, NH}_3}^{\text{Expt}} + \Delta H_{\text{f, H}_2\text{O}}^{\text{Expt}} - \Delta H_{\text{f, H}_2}^{\text{Expt}} - \Delta H_{\text{Rxn (1)}}^{\text{Calc}} \quad (4)$$

$$\Delta H_{\text{f, NH}_2\text{OH}} = \Delta H_{\text{f, NH}_3}^{\text{Expt}} + \Delta H_{\text{f, H}_2\text{O}_2}^{\text{Expt}} - \Delta H_{\text{f, H}_2\text{O}}^{\text{Expt}} - \Delta H_{\text{Rxn (2)}}^{\text{Calc}} \quad (5)$$

$$\Delta H_{\text{f, H}_2\text{O}_2} = 2 \Delta H_{\text{f, H}_2\text{O}}^{\text{Expt}} - \Delta H_{\text{f, H}_2}^{\text{Expt}} - \Delta H_{\text{Rxn (3)}}^{\text{Calc}} \quad (6)$$

The choice of isodesmic reaction is important to obtain accurate values. Although there are 5 single bonds on the reactant side (1 H-H, 1 O-H, **1 N-O**, 2 N-H) and on the product side (3 N-H, 2 O-H) in reaction (1), the N-O bond on the reactant side is not balanced by a similar  $\sigma$  bond on the product side. Reaction (3) is similar to (1) in terms of bond balance with the O-O bond unbalanced on the reactant side. In Reaction (2), there are 6 single bonds on the reactant side (3 O-H, **1 N-O**, 2 N-H) and on the product side (3 N-H, 2 O-H, **1 O-O**), but here the N-O bond is balanced better by the O-O bond on the product side. A better bond balance should result in a more effective cancellation of errors, and therefore, Reaction (2) should yield a more accurate value for  $\Delta H_{\text{rxn}}^{\text{Calc}}$  than Reaction (1) at the same level of theory. Thus we expect similar errors in the heat of formation values calculated using Reactions (1) and (3), and faster convergence with increasing level of theory for Reaction (2). In addition, agreement between values obtained from Reactions (1) and (2) can serve as an indicator that the theory is adequate to model the system.

The difference between the values calculated using Reaction (1) and (2) can be taken as a guide for selecting theories performing well for the system. The calculated values that exhibited a difference of 1 kcal/mol or less were considered acceptable values and are summarized in Table 1. Based on our calculations we recommend a value of  $-11.4 \pm 0.6$  ( $2\sigma$ ) kcal/mol for HA heat of formation at 1 atm and 298.17 K. The methods employed for obtaining the average value have an average deviation of  $\sim 1.1$  kcal/mol from the experimental value.

Table 1: Accurate values for HA heat of formation

Theory	Basis set	Mean Average Deviation	NH <sub>2</sub> OH		H <sub>2</sub> O <sub>2</sub>
			Heat of formation (kcal/mol)		
			Rxn (1)	Rxn (2)	Rxn (3)
G2		1.2	-11.78	-11.53	-32.83
G2MP2		1.6	-11.69	-11.67	-32.60
G3		1.0	-11.15	-11.28	-32.46
G3MP2B3		1.13	-11.88	-11.45	-33.01
G3B3		0.93	-11.51	-11.35	-32.74
CBS-Q		1.0	-12.18	-11.16	-33.60
CCSD(T)	cc-pVQZ	-	-11.56	-10.61	-33.52
	Average	1.1	-11.7	-11.4	-32.9
	St. dev.	0.3	0.3	0.3	0.4
	Experimental			-9.6 <sup>8</sup>	-32.58 <sup>7</sup>

#### Investigation of homogeneous catalysis of HA

The aim of studying elementary reactions of HA decomposition is to understand the initiation steps leading to HA runaway reactions and explosive behavior. Such an understanding of the behavior of HA at the molecular level would lead to development of better inhibitors to prevent metal catalysis, and consequently thermal runaway reactions.

Thermodynamic calculations for the plausible steps were being computed with the B3P86<sup>9</sup> density functional model and the cc-pVDZ<sup>10</sup> basis set, and a few of the elementary reactions investigated are summarized in Figure 1. The N-O bond strength is estimated to be ~ 72 kcal/mol and does not indicate instability due to the bond. The dimerization of hydroxylamine was not considered further because experimental results do not suggest a possible polymerization reaction. We have generated a plausible set of thermodynamically consistent elementary reactions, which are also in agreement with the observed product spectrum.

The catalytic behavior of HA will also be investigated by probing potential reaction pathways in the presence of ferrous (Fe<sup>2+</sup>) ions. The Stuttgart basis set<sup>11</sup> will be employed for modeling the Fe<sup>2+</sup> ion. A few of the elementary reactions involving HA and Fe<sup>2+</sup> are summarized in Figures 2a, 2b and 2c. None of the steps investigated so far have indicated initiation steps leading to explosive decomposition. We are continuing to investigate the probable causative event for HA catalysis in presence of metals ions.

Figure 2a: Probable elementary reactions of HA in presence of  $\text{Fe}^{2+}$

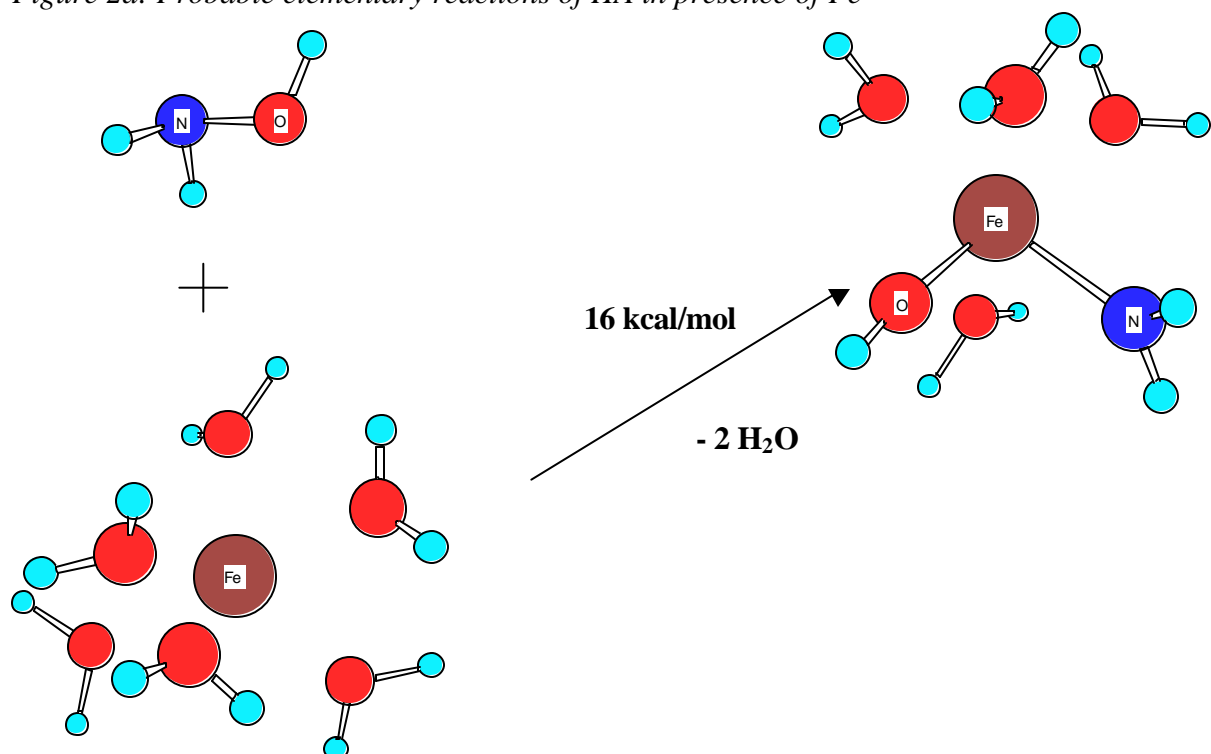


Figure 2b: Probable elementary reactions of HA in presence of  $\text{Fe}^{2+}$

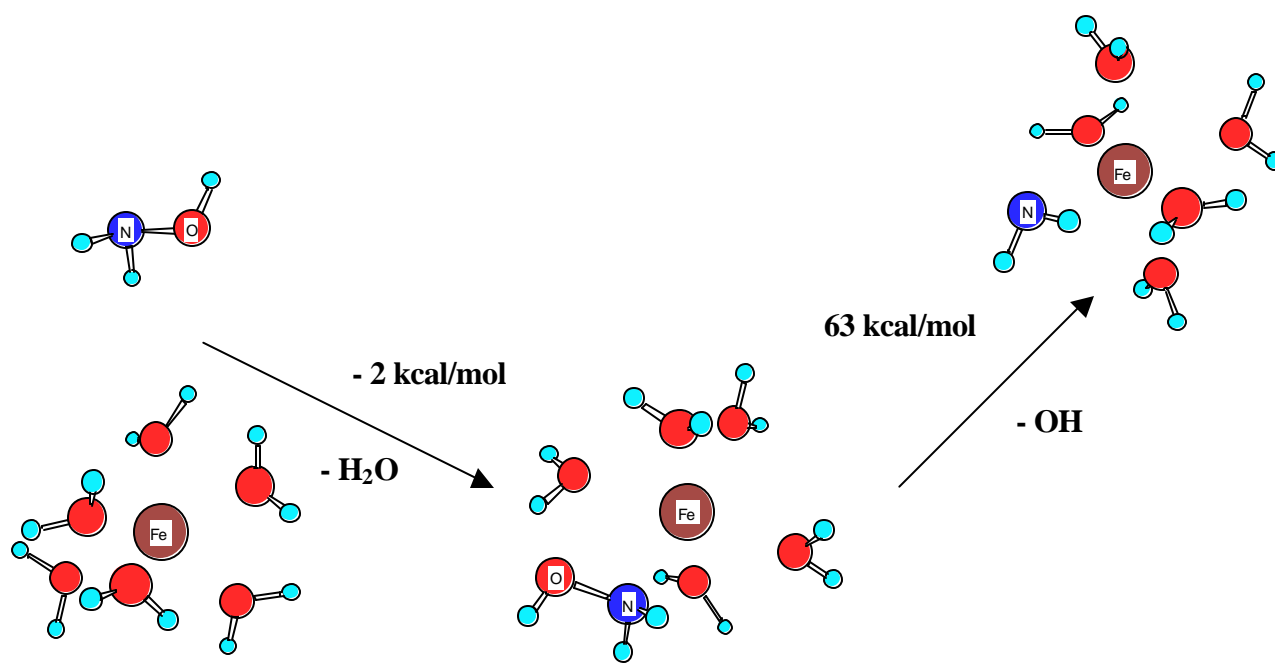
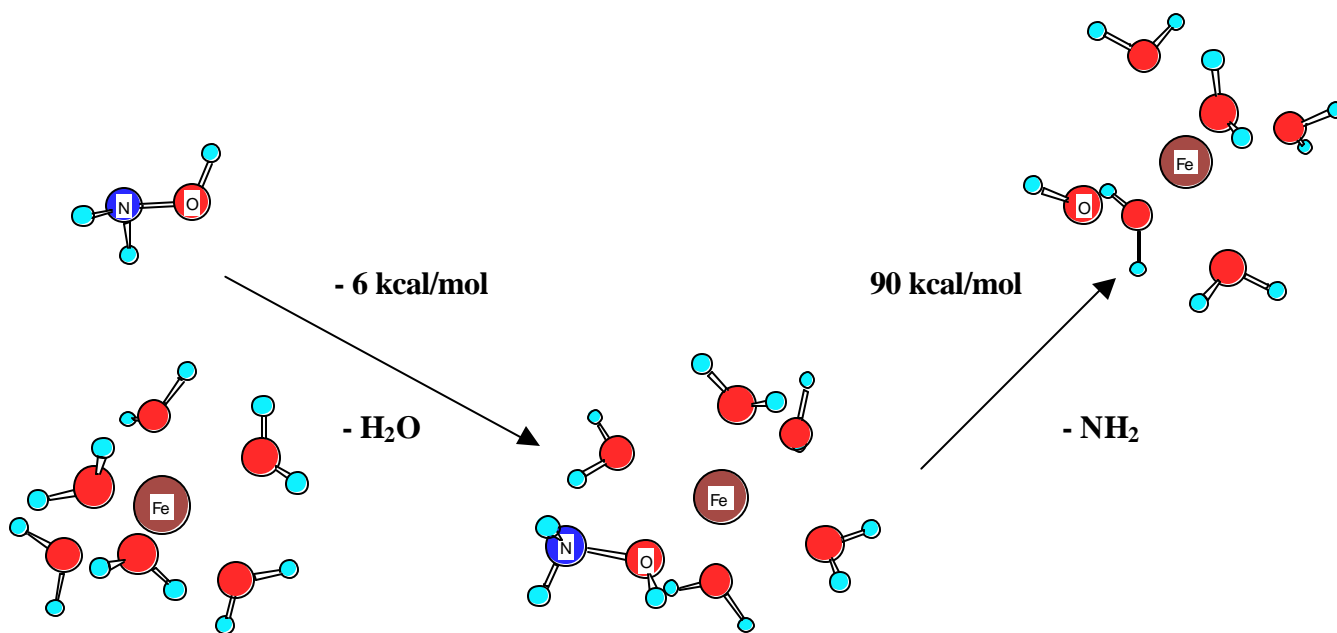


Figure 2c: Probable elementary reactions of HA in presence of  $Fe^{2+}$



### Prediction of calorimetric data

Information about the amount and rate of energy released can be obtained by performing calorimetric tests on the compound. Before a detailed calorimetric analysis is performed, the chemicals are screened by employing relatively less resource consuming techniques such as a Differential Scanning Calorimeter (DSC). There are many commercial calorimeters available in the market for screening or detailed testing.

Calorimetric measurements to determine reactivity can be resource consuming, so computational methods to predict reactivity hazards present an attractive option. There are certain rules of thumb commonly employed for estimating reactive hazards. For example, the presence of a nitro ( $NO_2$ ) group is regarded as a potential source of reactivity. The ASTM CHETAH program<sup>12</sup> is popular software that calculates certain thermodynamic parameters and classifies a composition as hazardous or non-hazardous. However the program provides no insight into process conditions to be avoided or information about the sensitivity of compounds to reaction initiation.

None of the available theoretical methods address the issue of chemical kinetics within a system that affects the rate of energy release and consequently the hazards posed by the substance. It is well known that the structure of a substance affects its reactivity<sup>13</sup> and this reactive nature of a compound is reflected in the calorimetric data. Therefore, our aim is to develop theoretical methods to quantify both kinetics and thermodynamic based on molecular structure alone.

To predict reactivity of a substance it is intuitive to deduce probable reaction pathways, but it is difficult to predict the reaction pathways for a compound, especially at

high temperatures<sup>14</sup>. Also it is difficult to extract exact kinetics from calorimetric data, since the calorimetric data on a substance reflects only temperature vs. time behavior. Therefore, we are developing prediction techniques for calorimetric data namely  $T_{\text{onset}}$  (kinetic parameter) and energy of reaction (thermodynamic quantity) based on molecular structure alone that exclude extensive kinetic modeling.

The exothermic behavior of a substance is influenced by the presence of functional groups, which also forms a basis for reactivity classification<sup>13,15,16</sup>. This leads us to believe that there is an inherent structure-property relationship between the observed calorimetric properties and molecular structure. For example, as mentioned earlier, the presence of nitro group ( $\text{NO}_2$ ) can be considered a potential source of reactivity. However, this dependence of observed behavior and molecular structure has not been satisfactorily quantified.

### Quantitative Structure Property Relationships (QSPR)<sup>17</sup>

The quantitative structure-property relationship (QSPR) techniques are a popular tool for correlating observed values based on molecular properties. QSPR techniques have been successfully employed for drug design and for correlating physical properties such as boiling point, autoignition temperature, and molecular properties. In addition to providing a means of predicting a property, a QSPR study may also lead to better understanding of structural features affecting the observed data. Our aim is to correlate and predict DSC calorimetric data.

We built a Quantitative Property Structure Relationship (QSPR) study table to develop the correlation. The first column of this table is either  $T_{\text{onset}}$  or energy of reaction, obtained from calorimetric experiments and is called the dependent variable. The remaining columns are the independent variables (characteristic of the molecules) called descriptors, which are characteristics of a molecule and account for the chemical structure of the molecule. A descriptor value can be obtained by experimental measurement or calculated based on molecular structure. We have used calculated descriptors to facilitate property predictions for unknown molecules. Following are a few of the descriptors we employed to correlate calorimetric data:

- a. Highest occupied molecular orbitals (HOMO)
- b. Lowest unoccupied molecular orbitals (LUMO)
- c.&d. Highest positive charge (HPC) and highest negative charge (HNC)
- e. Weakest bond (WB)
- f. Mid-point potential ( $V_{\text{mid}}$ )
- g. Delocalizability index ( $S_r$ )
- h. Charge – bond strength descriptor ( $x$ )

The descriptor values were obtained using the B3P86<sup>9</sup> density functional model and the cc-pVDZ<sup>10</sup> basis set. To keep the method computationally inexpensive, higher levels of theory were not tested at this stage of the project. The details of the descriptors used are available on request. Further statistical calculations were performed using the Statistical Analysis System (SAS, version 6.0)<sup>18</sup>.

Based on statistical analysis of the 19 nitro compounds<sup>19</sup>, we recommend the following equation for  $T_{\text{onset}}$ :

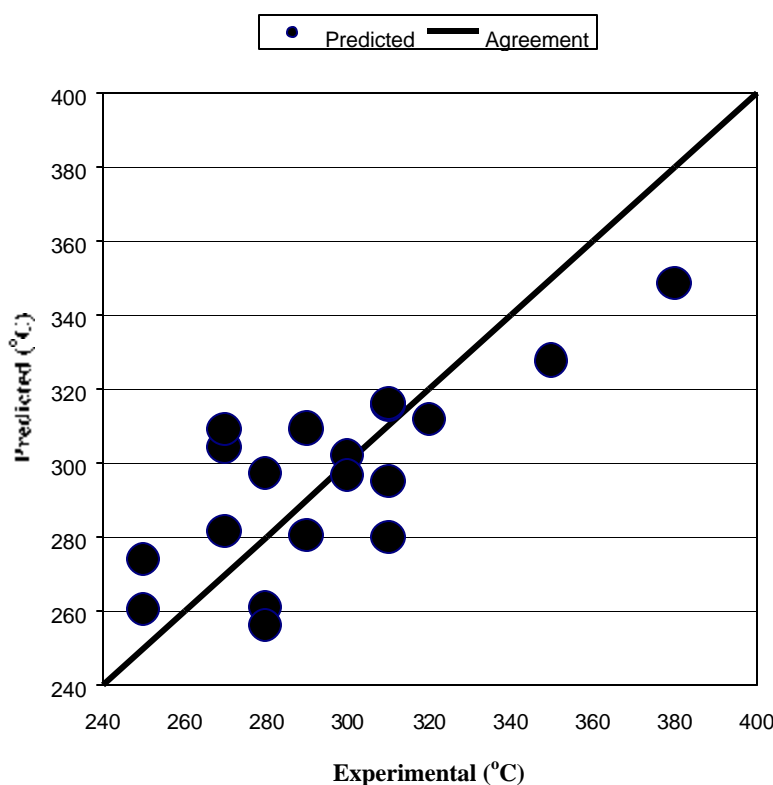
$$T_{\text{onset}} (\text{deg C}) = 827.0 - 1035.8 * \text{HPC} - 4.4 * \text{Sr} - 5.1 * \text{Dipole}$$

The predicted onset temperature values with an absolute average aggregate error of 6% and a bias of -0.5 % are plotted against the experimental values in Figure 3.

For the energy of reaction we obtain a simple relationship:

$$\text{Energy of reaction } [-DH] (\text{kcal/mol}) = 75 * \text{Number of nitro groups}$$

Figure 3. Predicted onset temperatures



### Future areas of research

The final goal of the above project is to develop computerized prediction tools for calorimetric data based on molecular structure alone and thus expedite reactive hazard assessment. As a next step, we intend to generate molecular descriptors for a variety of energetic materials, followed by statistical analysis, such as natural clustering, to obtain significant parameters characterizing energetic materials. We believe that such an approach will help decipher the molecular imprint of energetic materials and will aid in hazard identification.



## Conclusions

Molecular modeling techniques are especially important for modeling energetic materials and better understanding the reactive behavior. Theoretical methods are especially important to characterize and study energetic materials because of experimental difficulties. The methods described in this paper are applicable to other energetic materials. Prediction of calorimetric data provides an alternate route of obtaining data for reactive hazard assessment and can be developed into a computational screening program.

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